PATENT SPECIFICATION

NO DRAWINGS

1,047,694

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Date of Application and filing Complete Specification: Aug. 1, 1963.
No. 30562/63.
Application made in United States of America (No. 213,906) on Aug. 1, 1962.
Complete Specification Published: Nov. 9, 1966.

Index at acceptance:—D1 P(A1, A12, A17, B2A1, B2A2, B2B1, B2BX, B5A, B5B, B5C, C1AX, C2A10, C2A12A4, C2A12A10, C2A12B2, C2C1, C2C4, C2C7, C2C9)

Int. Cl.:—D 06 m

COMPLETE SPECIFICATION

Improvements in the Treatment of Cellulosic Fabrics

We, JOHNSON & JOHNSON, a Corporation organised under the laws of the State of New Jersey, United States of America of 501, George Street, New Brunswick, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to processes for treating fabrics consisting of or containing cellulosic fibres whereby such fabric is rendered shrinkage- and wrinkle-resistant and possesses a soft finish and a smooth appearance after laundering without subsequent ironing whereby it is suitable for wash and wear applications.

Many textile treating agents have been used to treat fabrics consisting of or containing cellulosic fibres to create in them the properties and characteristics mentioned in the preceding paragraph. Probably the simplest and cheapest of these textile treating agents is formaldehyde. Unfortunately, formaldehyde is volatile at room temperature and the fumes given off during volatilization are highly irritating to personnel. Additionally, an objectionable, high-strength loss is observed in fabrics which have been treated with formaldehyde. Furthermore, the results obtained by the use of formaldehyde are not readily reproducible whereby the resulting properties and characteristics of the treated fabrics vary widely, not only from one batch to another batch but very often within the length of one batch, itself.

It has now been discovered that the addition of certain acetals to textile treating baths contain formaldehyde diminish or reduce to a minimum many of the undesirable characteristics generally associated with the use of the formaldehyde. Such acetals are prepared from certain aldehydes and any of a large number of alcohols by techniques now well known in the art.

The aldehydes which are used to form the acetals employed in the methods of this invention contain from 1 to 5 carbon atoms. Representative aldehydes are formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, valeraldehyde, glyoxal, acrylaldehyde, crotonaldehyde, propiolaldehyde, and mixtures thereof. Aldehydes having more than 5 carbon atoms are generally unsuitable for use in the methods of this invention. If it is desired to use formaldehyde as the preferred aldehyde, various materials such as paraformaldehyde, formalin, trioxane, methylal, and similar formaldehyde-containing or formaldehyde-generating compounds may be used as sources of formaldehyde.

Suitable alcohols which may be reacted with the above-mentioned aldehydes to form acetals useful in this invention are methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, dibutylene, glycols, polyalkylene glycols, methoxyethanol, ethoxyethanol and other ethylene, propylene or butylene glycol monoethers, methoxyethoxy ethanol, polyhydric alcohols such as glycerlo, erythritol, dulcitol, mannitol and sorbitol, and partial ethers of such polyhydric alcohols.

According to the present invention, in the aforesaid alcohols used to prepare the acetals, the aliphatic monohydric alcohols contain from 1 to 5 carbon atoms; the alkylene glycols contain an alkylene radical having from 2 to 4 carbon atoms in a straight chain; and the aliphatic polyhydric alcohols contain from 3 to 6 hydroxyl groups and from 3 to 6 carbon atoms in the molecule. The term "alkylene" as used herein is understood to include a doubly unsatisfied aliphatic radical containing a substituted or unsubstituted straight chain as aforesaid, having its unsatisfied valences on either adjacent or separated carbon atoms.

Suitable monomeric acetals useful in this invention are di(hydroxyethoxyethyl) formal, di-(methoxyethoxyethyl) formal, di-(methoxy-

[Price 4s. 6d.]

ethyl) formal, di-(hydroxyethyl) formal, glyoxal tetramethyl acetal, glyoxal tetraethyl acetal, glyoxal tetrabutyl acetal, and mixed acetals such as methyl methoxyethyl formal, glyoxal dibutyl dimethoxyethyl acetal, or methyl hydroxyethoxyethyl formal or mixtures thereof.

The polymeric acetals which are useful in this invention are reaction products between an aldehyde and an alkylene or polyalkylene glycol. Typical polymeric acetals may be prepared from diethylene glycol and formaldehyde; ethylene glycol and formaldehyde; diethylene glycol, formaldehyde and glyoxal; diethylene glycol, sorbitol and formaldehyde; and diethylene glycol and acetaldehyde.

In general, those polymeric acetals which have proved useful in this invention may be made starting with ethylene glycol, a propylene glycol, a butylene glycol, dipropylene glycol, dibutylene glycols, polyalkylene glycols, mixtures thereof, or their mixtures with diethylene glycol which are reactive with formaldehyde or other aldehydes containing 1 to 5 carbon atoms to form water soluble products or products which are dispersible in water, either alone or with the aid of appropriate adjuvants. Polyalkylene glycols, such as diethylene glycol, triethylene glycol, tetraethylene glycol and tripropylene glycol may also be used, either alone or in admixture with the aforementioned glycols. Likewise, polyols, such as glycerine, pentaerythritol and sorbitol, may be added to the alkylene glycols in amounts up to about 50 mole per cent of the glycols for reaction with the aldehyde for forming water soluble or water dispersible products.

It is desirable that the alcohols used in this invention, when reacted with the aldehyde selected, should produce an acetal condensation product that is relatively non-volatile at a curing temperature of at least 125°C. (257°F.). In other words, it is advisable that the components of the acetal should be such as to produce a condensation product having a boiling point of above 125°C. (257°F.).

Of the acetals which have been indicated as useful in the method of this invention, the preferred compounds are the polymeric acetals derived from one of the specified aldehydes and at least one dialkylene glycol in which the alkylene radical has 2 to 4 carbon atoms in a straight chain. Each molecule of these acetals contains at least two dioxyalkylene radicals derived from the glycol and at least two alkylidene radicals derived from the aldehyde.

The most satisfactory acetals have been found to be those formed from diethyleane glycol and formaldehyde, the molecular weight of the polyformal so produced being approximately 500.

The formaldehyde and the acetal are normally applied to the fabric in an aqueous bath. Substantially any type of conventional impregnating or saturating apparatus can be used. Dip or immersion devices are preferred inasmuch as such provide the impregnation and saturation most satisfactory for the present invention. The excess textile treating agent is preferably removed by squeezing in a nip, or by blades or bars.

The concentration by weight of the formaldehyde in the aqueous treating bath is relatively low and is in the range of from 0.1% up to 5%. Within the more commercial aspects of the present invention, concentrations by weight of from 0.3% up to 3% are preferred.

In a similar way, the concentration of the acetal is relatively low in the aqueous treating bath. Concentrations by weight of from 1% up to 10% are used. Within the more commercial aspects of the present invention, acetal concentrations by weight of from 1.5% up to 7% are found preferable.

The amount of wet pick-up is controlled, such as by adjustable nip rolls, and depends upon many factors, notably the concentration of the formaldehyde and acetal in the treating bath. Normally, however, a wet pick-up of from 50% to 300%, by weight, based on the weight of the material being treated, is employed, with a preferred range extending from 75% to 150%, with optimum results at 100%.

In addition to the formaldehyde and the acetal, the padding bath may also contain acidic type catalyst which is operative during the curing step. Magnesium chloride is preferred because of its low tendency to tender the cellulosic material. Other acidic catalysts such as zinc chloride, zinc nitrate, zinc fluoborate, maleic anhydride, oxalic acid, ammonium chloride, ammonium thiocyanate, citric acid, tartaric acid, phosphoric acid, ethyl acid phosphate, ammonium sulphate and sodium bisulphate may be used.

The catalyst should be present in an amount of 5% to 200% by weight, based on the weight of the acetal in the bath.

The aqueous treating bath may be modified by the addition of a small amount of a relatively weak acid such as boric acid or acetic acid. Such an acid may be added in an amount ranging from 0.05% to 2%, by weight, based on the weight of the textile treating formulation. The addition of such acid aids the crosslinking reaction without unduly lowering the fabric strength. The benefits of such an addition are especially noticeable under high velocity drying conditions such as found in commercial drying units. Such a speeding up of the curing process without adversely affecting tear strength is extremely desirable. Finally, because of the increased speed of the crosslinking reaction between the cellulose and the formaldehyde, the amount of formaldehyde which is volatilized is decreased.

The impregnated fabric may then be framed, such as in a clip tenter frame, and dried, suitably at temperatures ranging from

212°F. up to 250°F. Curing is effected by heating, preferably at temperatures of from 250°F. to 350°F., for periods ranging in typical cases from 10 minutes to 1/2 minute. The time of the cure varies inversely with the temperature. It is to be appreciated that, although drying and curing are described herein as two separate procedural steps, they may be combined into a single step, in which the temperatures used may suitably be from 250°F. to 350°F., with preferred temperatures from 290°F. to 310°F.

After curing, the fabric may be washed lightly in an aqueous medium containing a detergent and a mild alkali, rinsed thoroughly and dried. Since the finish is non-resinous, the finish hand is quite soft. Stiffness, if desired, may be obtained by the use of stiffening agents such as starch, polyvinyl alcohol or polyvinyl acetate.

The amount of dry add-on or the percentage of increase in the weight of the treated fabrics as a result of the cross-linking reaction depends naturally upon the amount of wet pick-up and upon the concentration of the formaldehyde and the acetal in the aquetous textile treating bath. This percentage of increase in weight is kept within certain ranges so as to provide sufficient interaction or cross-linking of the cellulose with the formaldehyde and the acetal condensation product to produce the desired properties and characteristics.

An increase in weight of the fabric treated by the methods of this invention of from 1% to 15% based on the dry weight of the untreated fabric produces satisfactory results. Within the more commercial aspects of the present invention, however, an increase in weight of from 2% to 10% has been found preferable. These increases in weight are caused by the interaction or cross-linking of both the formaldehyde and the acetal condensation product with the cellulosic material. Increases in weight due to the retention of catalysts and hand modifying agents in the cellulosic material are not included in the values specified.

The invention will be further illustrated in greater detail by the following specific examples I to IV. It should be understood, however, that although these examples I to IV may describe in particular detail some of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not to be construed as limited thereto.

EXAMPLE I.

The basic procedure comprises the application of the selected formulation to the cellulosic fabric by means of a conventional padder, using a single dip and a single nip. The wet pick-up is adjustably controlled to approximately 100% by the weight of the cellulosic fabric being treated.

After the selected formulation is applied to the cellulosic fabric, drying and curing take place. The fabric is framed in a clip tenter frame to its original dry dimensions and dried at a temperature of 250°F. for a period of 5 minutes. Curing takes place in forced hot-air ovens at a temperaturea of 325°F. for a period of 2½ minutes. The treated fabric is then washed lightly in water containing a detergent and a mild alkali to remove the catalyst and any unreacted polyacetal. The fabric is again dried on a tenter frame and is then ready for testing.

Appearance is rated as follows: the fabric is given one conventional household wash and are line-dried. Ratings are visual and subjective. The ratings are: excellent; good; fair; and poor.

The degree of wrinkle resistance is measured on a standard Monsanto Wrinkle Recovery Instrument which measures the angular recovery of the test fabric which has been creased in half by a definite weight for a given time at a standard temperature and humidity. A 180° recovery is perfect but such a fabric probably does not drape well nor take good pleats or creases. Good wrinkle recovery values (average of warp and filling) range from 110° to 130°, with excellent ratings for the range from above 130° to 145°. For further details of this testing procedure, see AATCC Tentative Test Method 66-1959 and ASTM Designation: D1295-53T.

The fabric is a 48x44, 40-inch wide, bleached cotton fabric measuring 3.75 yards per pound. The formulations contain an acetal but no formaledhyde and are as follows, with parts being expressed by weight.

Formulation	Sample Numbers					
	13	14	15	16	17	18
Water	30	30	30	26	26	26
12% Polyvinyl Alcohol	50	50	50	50	50	50
70% Diethylene glycol formal	12	12	12	16	16	16
37% Formaldehyde	0	0	0	0	0	0
50% $MgCl_2.6H_2O$	8	8	8	8	8	8

These samples are given 1 hot Bendix wash and tested for appearance. The results are as follows:

13	14	15	16	17	18
Poor	Poor	Fair	Poor	Poor	Poor

Sample 16 is tested for wrinkle resistance. The results are as follows:

Original	Warp	83°	
	Filling	84°	
	Average	84°	Not Acceptable
After 1 Commerical Wash	Warp	102°	
	Filling	101°	
	Average	102°	Not Acceptable
After 5 Commercial Washes	Warp	95°	
	Filling	97°	
	Average	96°	Not Acceptable
After 10 Commercial Washes	Warp	88°	
	Filling	94°	
	Average	91°	Not Acceptable

It is apparent from these results that the use of diethylene glycol formal, per se, that is, without the addition of formaldehyde, does not produce a satisfactory or acceptable wrinkle-resistant fabric suitable for wash and wear applications.

Additional samples of the same fabric used previously in this Example are treated with the following formulations containing both an acetal and formaldehyde, with parts being expressed by weight.

Formulation	Sample Numbers					
	22	23	24	25	26	27
Water	26	26	26	24	24	24
12% Polyvinyl Alcohol	50	50	50	50	50	50
70% Diethylene glycol formal	12	12	12	12	12	12
37% Formaldehyde	4	4	4	4	4	4
50% $MgCl_2.6H_2O$	8	8	8	8	8	8

Very little odour of formaldehyde is noted during the treatment of the fabric with the formaldehyde - containing formulation, and there is practicaly no formaldehyde odour noted during subsequent handling and processing of the fabric. The fabric has good dimensional stability and is non-chlorine retentive.

These samples are given 1 hot Bendix wash and tested for appearance. The results are as follows:

22	23	24	25	26	27
Good	Good	Good	Fair	Good	Good

Sample 25 is tested for wrinkle resistance. The results as are follows:

Original	Warp	104°	
	Filling	114°	
	Average	109°	Acceptable
After 1 Commercial Wash	Warp	114°	
	Filling	109°	
	Average	112°	Good
After 5 Commercial Washes	Warp	122°	
	Filling	116°	
	Average	119°	Good
After 10 Commercial Washes	Warp	122°	
	Filling	118°	
	Average	120°	Good

It is apparent from these results that the use of diethylene glycol formal in combination with formaldehyde produces a satisfactory and acceptable wrinkle-resistant fabric suitable for wash and wear applications.

EXAMPLE II

The procedures set forth in Example I are followed substantially as set forth therein with the exception that the formulation is different and comprises the following constituents:

Formulation	Weight	(Parts by Weight)
Water	275 pounds	55
Liquid Starch Stiffener	125 pounds	25
70% Diethylene glycol formal	30 pounds	6
37% Formaldehyde	30 pounds	6
50% $MgCl_2.6H_2O$	40 pounds	8
Vat Pigment Dyestuff	19 grams	<0.01

Very little odour of formaldehyde is noted during the treatment of the fabric with the formaldehyde-containing formulation, and there is practically no formaldehyde odour noted during subsequent handling and processing of the fabric. The fabric is dimensionally stable and is non-chlorine retentive.

The wrinkle recovery results are as follows:

Original	120°
After I Hot Bendix Wash	124°
After 5 Commercial Washes	122°
After 10 Commercial Washes	122°

The percent shrinkages are as follows:

	Warp	Filling
After 1 Sanforizing Wash	—1.1	—0.3
After 1 Commercial Wash	—0.9	+0.1
After 5 Commercial Washes	—1.2	—0.4
After 10 Commercial Washes	—1.4	—0.5

The pH of the acid sour is 3.5 in these commercial washes. This indicates outstanding resistance to acid hydrolysis.

The treated fabric possesses good wrinkle recovery and good shrinkage resistance. It has good dimensional stability, is non-chlorine retentive, and is suitable for use in wash and wear application.

EXAMPLE III

The procedures set forth in Example I are followed substantially as set forth therein with the exception that the fabric used is a 88x80, 40-inch wide, combed cotton lawn, dyed black, measuring a 6.90 yards per pound. The textile treating formulations are also different, containing an acetal but no formaldehyde, and are as follows:

Formulation	Sample Numbers				
	1	2	3	4	5
Water	90	88	86	84	82
70% Diethylene glycol formal	2	4	6	8	10
37% Formaldehyde	0	0	0	0	0
50% $MgCl_2.6H_2O$	8	8	8	8	8

These samples are given 1 standard household wash (G.E. Filter-Flo Washer), spin dried and then tested for appearance. All samples were rated: "Poor".

The conclusion is therefore again reached that the use of diethylene glycol formal, per se, that is, without the addition of any formaldehyde, does not produce a satisfactory or acceptable wrinkle-resistant fabric suitable for wash and wear applications.

Additional fabric samples are treated with the following formulations containing both formaldehyde and an acetal:

Formulation	Sample Numbers				
	6	7	8	9	11
Water	87	86	85	84	100
70% Diethylene glycol formal	4	4	4	4	0
37% Formaldehyde	1	2	3	4	0
50% $MgCl_2.6H_2O$	8	8	8	8	0

Very little odour of formaldehyde is noted during the treatment of the fabric with the formaldehyde-containing formulation, and there is practically no formaldehyde odour noted during subsequent handling and processing of the fabric. The fabric possesses excellent dimensional stability and is non-chlorine retentive.

These samples are given 1 standard household wash (G.E. Filter-Flo Washer), spin dried and tested for appearance. The results are as follows:

6	7	8	9	11
Fair	Good	Good	Excellent	Poor

The samples are also tested for wrinkle recovery after 1 Sanforized wash. The results are as follows:

	6	7	8	9	11
Warp	115°	122°	118°	124°	90°
Filling	132°	128°	128°	142°	112°
Average	124°	125°	123°	133°	101°

All four treated samples are acceptable. The blank (Sample 11) is not acceptable.

The conclusion is again reached that the combination of the acetal condensation product and formaldehyde produces a satisfactory and acceptable wrinkle-resistant fabric suitable for wash and wear applications.

EXAMPLE IV

The procedures set forth in Example I are followed substantially as set forth therein with the exception that the formulation is different and comprises the following constituents:

Formulation	Parts by Weight
Water	30 gallons
Liquid Starch Stiffener	100 pounds
Heat to 100°F, and hold at that temperature for 10 minutes.	
Water	52 gallons
70% Diethylene glycol formal	60 pounds
37% Formaldehyde	60 pounds
50% $MgCl_2.6H_2O$	80 pounds
56% Acetic Acid	2 pounds
Softening Agent	10 pounds
Vat Pigment Dyestuff	36 grams

Very little odour of formaldehyde is noted during the treatment of the fabric with the formaldehyde-containing formulation and there is practically no formaldehyde odour noticed during subsequent handling and processing. The fabric is dimensionally stable and is non-chlorine retentive. The tear strength is extremely good and there is no tendering of the fabric. Additionally, the curing process is speeded up as follows:

Temperature	Time
330°F.	1.5 minutes

The sample is found satisfactory and is suitable for use as a wash and wear resilient interlining in shirt collars and shirt cuffs.

EXAMPLE V (*contrasting procedure described for purposes of comparison*)

The procedures of Example I are followed substantially as set forth therein with the exception that the following formulation containing formaldehyde but no acetal is used:

Formulation	Parts by Weight
Water	56
30% Starch ether stiffener	30
Acetal	0
37% formaldehyde	6
50% $MgCl_2.6H_2O$	8

The original wrinkle recovery is only 86° which is unacceptable. The process is repeated several times and the wrinkle recovery values determined for the treated fabric. Some values are as low as 70° and others up to 118°. The unreliability of such results is apparent. The tear strength results are similarly variable. Some results show: 0.56 pounds Elmendorf tear vs. 0.74 pounds Elmendorf tear for a standard fabric. When such tests are repeated, reproducibility is extremely poor and unreliable.

Although woven fabrics are described in particularity, it is to be appreciated that the

principles of the present inventive concept are equally applicable to other forms of fabricated products such as nonwoven fabrics and knitted fabrics.

Although cotton and viscose rayon have been referred to in this description of the invention as the preferred cellulosic fibres, it is to be appreciated that other cellulosic fibres can be used. Illustrative of such other fibres are flax, ramie, sisal and hemp. It is also to be noted that other fibres such as nylon 6, nylon 6/6, acrylics, polyesters and cellulose esters, may be used in blends in varying proportions with the cellulosic fibres.

The words "Bendix" and "Sanforized" used in the foregoing Examples are registered Trade Marks.

WHAT WE CLAIM IS:

1. A process for treating fabrics consisting of or containing cellulosic fibres whereby said fabric is rendered shrinkage- and wrinkle-resistant and possesses a soft finish and a smooth appearance after laundering without subsequent ironing which comprises treating said fabric with a textiletreating bath comprising from 0.1 per cent to 5 per cent by weight of formaldehyde and from 1 per cent to 10 per cent by weight of an acetal derived from the condensation of an aliphatic aldehyde containing from 1 to 5 carbon atoms and an aliphatic hydroxy compound which is an aliphatic monohydric alcohol containing from 1 to 5 carbon atoms, a monoalkylene or polyalkylene glycol in which the alkylene radical has from 2 to 4 carbon atoms in a straight chain, methoxyethanol, ethoxyethanol or another ethylene, propylene or butylene glycol monoether, methoxyethoxyethanol, an aliphatic polyhydric alcohol containing from 3 to 6 hydroxy groups tnd from 3 to 6 carbon atoms in the molecule, a partial ether of such a polyhydric alcohol, or a mixture of the aforesaid aliphatic hydroxy compounds, and then heating the textile fabric to cure the acetal in situ in the textile fabric.

2. A process according to claim 1, in which the textile treating bath comprises from 0.3 per cent to 3 per cent by weight of formaldehyde and from 1.5 per cent to 7 per cent by weight of the acetal.

3. A process for treating fabrics consisting of or containing cellulosic fibres whereby said fabric is rendered shrinkage- and wrinkle-resistant and possesses a soft finish and a smooth appearance after laundering without subsequent ironing which comprises treating said material with a textile treating bath comprising from 0.1 per cent to 5 per cent by weight of formaldehyde and from 1 per cent to 10 per cent by weight of diethylene glycol formal, and then heating the textile fabric to cure the acetal in situ in the textile fabric.

4. A process according to claim 1 for treating fabrics consisting of or containing cellulosic fibres, using both formaldehyde and an acetal, substantially as hereinbefore described.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.